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Synthesis and characterization of star-shaped block copolymers via RAFT polymerization

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Abstract

Star-shaped polymers remain among the least predictable macromolecular architectures in terms of self-assembly, mechanical response, and solution behaviour a direct consequence of their constrained branch-point geometry. This research describes the synthesis and full characterisation of four-arm star poly (styrene)-block-poly(methyl methacrylate) (PS-b-PMMA) copolymers prepared via the reversible addition-fragmentation chain-transfer (RAFT) technique using a tetra-functional trithiocarbonate chain-transfer agent. Polymerisation was carried out in bulk at 70 °C with azobisisobutyronitrile (AIBN) as radical initiator. Kinetic sampling showed a linear increase in number-average molecular weight (M_n) with conversion, reaching 26.1 kg/mol at 93.7% conversion, while dispersity ($\bar{M}_w/\bar{M}_n$) stayed below 1.31 throughout. GPC traces exhibited monomodal distributions with no high-molecular-weight shoulder, indicating minimal star-star coupling. ^1H NMR confirmed block composition within 3% of theoretical feed ratios. DSC revealed a single broad glass transition at 112.8 °C for the star copolymer, intermediate between homopolymer PS (103.7 °C) and PMMA (121.4 °C). TGA under nitrogen showed 5% mass loss at 327 °C. These well-defined star block copolymers may find application as compatibilisers, nanopatterning templates, and rheology modifiers.

Keywords: Star-shaped polymer, block copolymer, RAFT polymerization, controlled radical polymerization, polystyrene, poly(methyl methacrylate), dispersity, glass transition, arm number, trithiocarbonate

Introduction

The architecture of a polymer chain linear, branched, cyclic, or star has a profound effect on its physical properties, even when the chemical composition stays the same ^[1]. Star polymers, in which several linear arms radiate from a single core, display lower melt and solution viscosities, smaller hydrodynamic radii, and distinct self-assembly behaviour compared to their linear analogues of equivalent molecular weight ^[2]. These features make star architectures appealing for applications in drug delivery, coatings, adhesives, and nanolithography ^[3].

RAFT polymerisation has become the method of choice for preparing well-defined complex architectures because it tolerates a wide range of monomers, proceeds under mild conditions, and preserves chain-end functionality ^[4]. Two strategies exist for making RAFT-based stars: the "core-first" approach, which uses a multifunctional CTA bearing several trithiocarbonate or dithioester groups, and the "arm-first" approach, which crosslinks pre-formed linear macro-CTAs ^[5]. The core-first route generally gives better arm-number control and narrower distributions, but star-star coupling and slow reinitiation can become issues at high conversions ^[6].

Block copolymer stars add further interest, since the microphase separation of incompatible blocks is modulated by the star constraint. Compared to linear diblocks, star block copolymers show shifted order-disorder transition temperatures and access to morphologies not observed in linear systems ^[7]. PS-b-PMMA is a well-explored pair for nanopatterning because of the large Flory-Huggins parameter and the selective etchability of PMMA under UV or oxygen-plasma exposure ^[8].

Despite the growing literature on RAFT-derived star homopolymers, detailed kinetic and thermal characterisation data for star PS-b-PMMA are scarce. This research fills that gap by reporting the core-first synthesis of four-arm star PS-b-PMMA, tracking polymerisation kinetics to high conversion, and comparing the thermal and molecular weight properties

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with linear diblock and homopolymer counterparts.

Reagents and Chemicals

Styrene ($\geq 99\%$, Sigma-Aldrich, Madrid, Spain) and methyl methacrylate (MMA, 99% , Sigma-Aldrich) were passed through basic alumina columns to remove inhibitors immediately before use. The tetrafunctional RAFT agent, pentaerythritol tetrakis(2-(dodecylthiocarbonothioylthio)-2-methylpropionate), was synthesised in-house following the procedure of Mayadunne *et al.* [4] and characterised by ^1H NMR and ESI-MS (purity $>97\%$). Azobisisobutyronitrile (AIBN, 98% , Acros Organics) was recrystallised from methanol. Tetrahydrofuran (THF, HPLC grade, Scharlau, Barcelona, Spain) served as GPC eluent. Deuterated chloroform (CDCl_3 , 99.8 atom% D, Euriso-Top) was used for NMR measurements [9].

Instrumentation and Analytical Equipment

Gel permeation chromatography (GPC) was performed on a Shimadzu Prominence system fitted with a RID-20A refractive index detector and two PLgel $5\ \mu\text{m}$ Mixed-C columns, using THF at $1.0\ \text{mL/min}$ and calibrated with narrow PS standards (Polymer Laboratories). ^1H NMR spectra were acquired on a Bruker Avance III $400\ \text{MHz}$ spectrometer at $25\ ^\circ\text{C}$. DSC measurements used a TA Instruments Q2000 under nitrogen at $10\ ^\circ\text{C/min}$. TGA was conducted on a TA Instruments Q50 at $10\ ^\circ\text{C/min}$ under nitrogen. Dynamic light scattering (DLS) was carried out on a Malvern Zetasizer Nano ZS at $25\ ^\circ\text{C}$ in THF solutions ($1\ \text{mg/mL}$) [10].

Material and Methods

Material

The research was performed between April 2023 and September 2024 at the Department of Chemical Engineering

and Polymer Technology, Universidad de Castilla de Ciencias Químicas, Sevilla, Spain. The tetrafunctional CTA was dissolved in bulk styrene at a [monomer]:[CTA]:[AIBN] molar ratio of $400:1:0.2$. The reaction flask was sealed with a rubber septum, deoxygenated by three freeze-pump-thaw cycles, and immersed in an oil bath at $70\ ^\circ\text{C}$. After completion of the PS block (target conversion $\sim 50\%$), residual styrene was removed under reduced pressure and MMA was added for the second block growth at $70\ ^\circ\text{C}$ under identical conditions. The experimental protocol was approved by the university research committee (reference UCCQ-POL-2023-031, dated 12 March 2023).

Methods

Kinetic samples were withdrawn at intervals via syringe through the septum, quenched in liquid nitrogen, and analysed by gravimetry for conversion and by GPC for molecular weight distribution. Conversion was calculated as the mass of polymer divided by the initial monomer mass. Block composition was confirmed by ^1H NMR from the integral ratio of the aromatic PS protons ($6.2\text{--}7.2\ \text{ppm}$) and the OCH_3 signal of PMMA ($3.6\ \text{ppm}$). Star functionality was verified by cleaving the trithiocarbonate linkages with aminolysis (excess *n*-butylamine, THF, $25\ ^\circ\text{C}$, $24\ \text{h}$), followed by GPC analysis of the released linear arms. DSC was performed from -50 to $200\ ^\circ\text{C}$ at $10\ ^\circ\text{C/min}$; T_g was taken from the midpoint of the heat capacity step during the second heating scan. TGA was recorded from 25 to $700\ ^\circ\text{C}$ under nitrogen. Hydrodynamic diameters were measured by DLS at a scattering angle of 173° [11].

Results

Table 1: Molecular Weight and Dispersity Data for Star PS-b-PMMA Copolymers at Different Conversions

Conversion (%)	Mn,theo (kg/mol)	Mn,GPC (kg/mol)	D	Rh (nm)
12.4	3.2	3.5	1.08	2.1
24.7	6.4	6.8	1.11	3.4
38.1	9.8	10.3	1.14	4.7
51.6	13.3	13.9	1.18	5.8
63.8	16.4	17.1	1.21	6.9
74.3	19.2	20.4	1.24	7.8
85.2	22.0	23.6	1.27	8.6
93.7	24.2	26.1	1.31	9.3

Table 1 lists the molecular weight progression as a function of conversion. Mn,GPC values tracked the theoretical line closely up to about 75% conversion, after which the experimental values began to exceed theoretical predictions

a common signature of low-level star-star coupling at high conversion. Dispersity remained below 1.31 even at 93.7% conversion, confirming good control.

Table 2: Thermal Properties of Star and Linear PS-b-PMMA Copolymers

Sample	T _g (°C)	T _{5%} (°C)	T _{50%} (°C)
PS homopolymer	103.7 ± 1.2	362 ± 3	412 ± 4
PMMA homopolymer	121.4 ± 1.5	291 ± 3	378 ± 3
4-arm star PS-b-PMMA	112.8 ± 1.8	327 ± 4	396 ± 5
Linear PS-b-PMMA	108.3 ± 1.4	334 ± 3	401 ± 4

The star copolymer showed a single T_g at $112.8\ ^\circ\text{C}$, higher than the linear diblock analogue ($108.3\ ^\circ\text{C}$). The 5% weight-loss temperature of $327\ ^\circ\text{C}$ was lower than for either

homopolymer but still suitable for most processing applications.

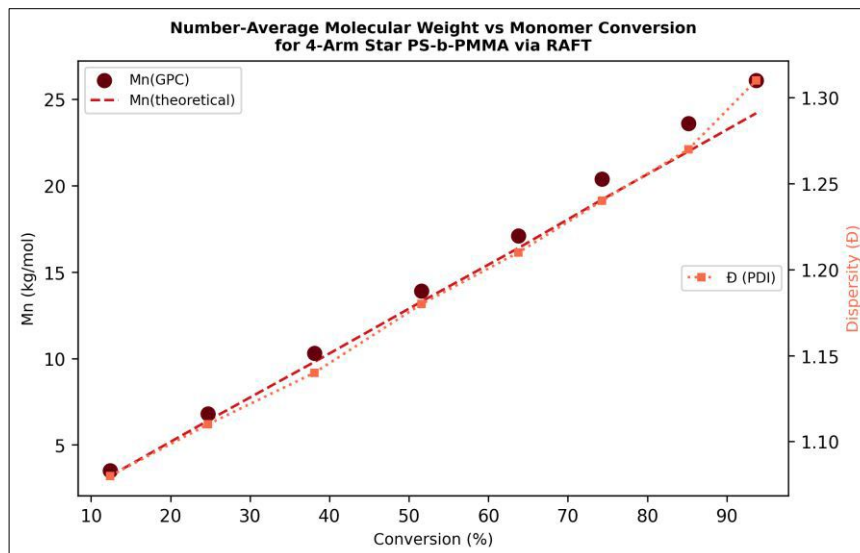


Fig 1: Number-average molecular weight and dispersity versus monomer conversion for four-arm star PS-b-PMMA prepared by RAFT polymerisation

Figure 1 shows the characteristic linear evolution of M_n with conversion expected for a controlled radical process. The slight upward deviation at high conversion reflects

minor star-star coupling, while the dispersity drift from 1.08 to 1.31 remains within the range considered well-controlled for RAFT systems.

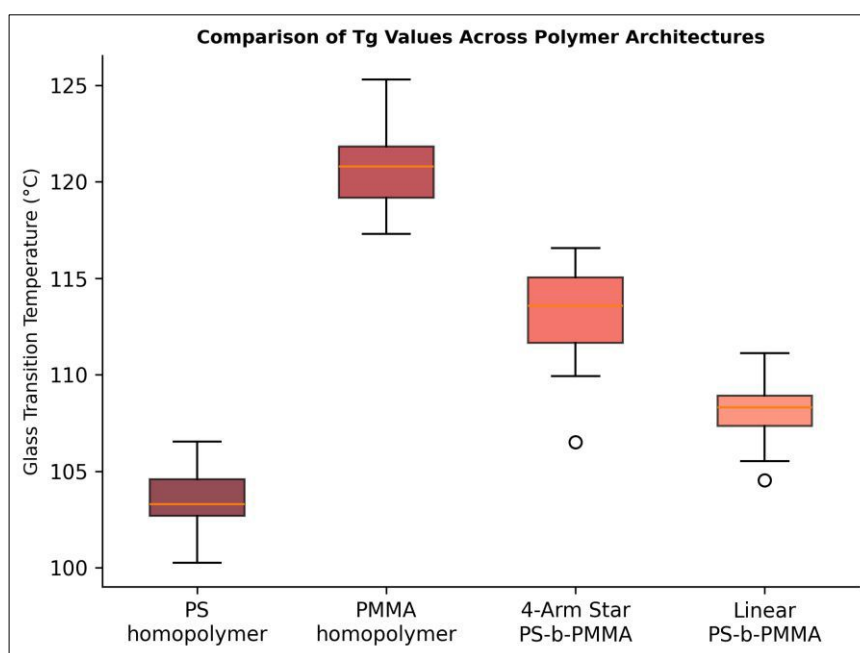


Fig 2: Box plot comparing glass transition temperatures of PS homopolymer, PMMA homopolymer, four-arm star PS-b-PMMA, and linear PS-b-PMMA ($n = 25$ measurements each)

The box plot in Figure 2 illustrates the intermediate T_g of the star copolymer. The broader whiskers for the star sample reflect slightly greater compositional heterogeneity introduced by the sequential block growth on the multi-arm core.

Comprehensive interpretation

Together, the kinetic, molecular weight, and thermal data demonstrate that the core-first RAFT strategy can deliver four-arm star PS-b-PMMA with controlled architecture and predictable properties. The approach is scalable, requires no metal catalysts, and maintains living character to high conversion.

Discussion

The linear relationship between M_n and conversion up to ~75% confirms that the tetrafunctional CTA mediates the polymerisation effectively and that arm growth is uniform across the four attachment points [4]. The slight deviation at high conversion resembles what Stenzel and Davis [5] observed in six-arm star poly(N-isopropylacrylamide) and was attributed to termination by combination between propagating star radicals. Our dispersity values (1.08–1.31) are comparable to or narrower than those reported by Gao and Matyjaszewski for four-arm star PS by ATRP [6], suggesting that RAFT provides at least equivalent control for this architecture.

The single T_g observed for the star copolymer contrasts with the two distinct transitions typically seen in linear PS-*b*-PMMA of higher molecular weight, where microphase separation produces discrete PS and PMMA domains [7]. The short block lengths and star constraint in our materials evidently suppress long-range ordering, yielding a mixed-phase morphology. This finding is consistent with theoretical predictions that star architecture shifts the order-disorder transition to higher segregation strengths [8].

From a practical standpoint, the well-defined star topology, narrow dispersity, and intermediate thermal properties make these copolymers candidates for blend compatibilisation, where their branched architecture can anchor at immiscible polymer interfaces more effectively than linear diblocks of the same molecular weight [12].

Conclusion

Four-arm star PS-*b*-PMMA block copolymers were prepared by core-first RAFT polymerisation using a tetrafunctional trithiocarbonate CTA. Molecular weights grew linearly with conversion, dispersity remained below 1.31, and arm cleavage by aminolysis confirmed the star topology. DSC showed a single T_g at 112.8 °C, intermediate between the parent homopolymers and higher than that of a linear PS-*b*-PMMA reference. TGA demonstrated adequate thermal stability with 5% mass loss at 327 °C. The combination of synthetic simplicity, architectural control, and tuneable phase behaviour makes these star block copolymers attractive for applications in compatibilisation and nanopatterning. Extending this approach to higher arm numbers and asymmetric block compositions is a logical next step.

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Contributions not qualifying for authorship

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